



## Review of diffusion–absorption refrigeration technologies



J.L. Rodríguez-Muñoz, J.M. Belman-Flores\*

Department of Mechanical Engineering, Engineering Division, Campus Irapuato-Salamanca, University of Guanajuato, Salamanca, Gto., CP.36885, Mexico

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### ABSTRACT

A review of diffusion–absorption refrigeration technologies has been done in this work in order to promote their main characteristics in terms of the refrigeration process, their applications, work fluids, current trends and limitations, among others. Over 70 publications in the field were analyzed concluding that diffusion–absorption technology represents a complementary and viable alternative in the field of refrigeration technologies for small cooling capacity, due to an increase in the current demand of refrigeration and air-conditioning devices.

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### 1. Introduction

In the last decades there has been an inevitable increase in the demand in refrigeration and air-conditioning devices to fulfill basic and comfort needs in different sectors of society. Refrigeration technology based on vapor compression is the leading technology in the world, which is an indirect cause of greenhouse effect gases due to the type of energy it uses. It consumes nearly 30% of the final energy in the world [1]. Furthermore, developing countries continue to use compression systems based on refrigerant fluids that damage the ozone layer, ODP, and represent a high global warming potential, GWP.

New technologies have emerged in response to the search for better alternatives that would not have damaging effects on the environment. These technologies are characterized by the type of activation energy, such as the use of renewable energy including solar, geothermal, residual heat, etc., which can be translated to a

reduction of greenhouse gas emissions, and the working fluids that they use do not contribute to global warming.

Among these technologies, refrigeration systems by absorption are the most commonly used for refrigeration and air conditioning applications [2], which ones have been demonstrated that under the same cooling capacity, the total energy consumed and total cost is less than a vapor compression system [3]. A large number of absorption refrigeration units have been designed and commercialized around the world with refrigeration capacities between 10 and 1000 kW [4]. Small capacity absorption refrigeration systems have problems in the solution pump which results in an inefficient performance of the device and therefore of the global system. Diffusion–absorption refrigeration systems have been developed as a response to such problems. This type of technology uses three working fluids in its refrigeration process, which are distinctive of this technology. Among these fluids are  $\text{NH}_3/\text{H}_2\text{O}/\text{H}_2$ , in which ammonia is used as a refrigerant, the water is used as an absorbent and hydrogen as an auxiliary gas.

The first diffusion–absorption refrigeration system was developed and patented in the 1920s [5] and since then millions of units

\* Corresponding author. Tel.: +52 464 6479940x2419; fax: +52 464 6479940x2311.  
E-mail address: [jfbelman@ugto.mx](mailto:jfbelman@ugto.mx) (J.M. Belman-Flores).

have been manufactured for domestic refrigeration devices, caravans, camps, recreational vehicles, hotel rooms and areas with no electricity.

The activation energy for these devices can come from liquefied gas (LPG), natural gas or kerosene. Even when these systems can run for numerous continuous hours, its application is limited to small capacity refrigerators. They have low efficiency; traditionally a refrigerator based on this technology provides a cooling capacity between 200 and 400 W, with a coefficient of performance, COP, between 0.2 and 0.25.

Therefore research has been done through the years in order to find significant increases in energy efficiency for domestic appliances [6–8], but the best COP that has been found is around 0.3 [9]. The bubble pump is among the most studied components of the diffusion–absorption systems, which is a critical component that has a positive effect in the energy efficiency of the system. Other studies show that geometric parameters and the characteristics of the flux regime are also factors that affect efficiency [10–15].

Based on the latter, the main objective of this work is to provide knowledge regarding the history and existing works based on diffusion–absorption refrigeration technology, its main characteristics, applications and trends as an alternate technology in the field of refrigeration and air-conditioning. This information will allow researchers and developers to understand and improve this technology, as well as provide greater impulse for it to be considered a viable alternative in this area.

## 2. Cooling process and components

Fig. 1 shows a schematic diagram of a diffusion–absorption refrigeration system (DAR). The main components of the DAR system are: generator/bubble pump, condenser, evaporator, solution heat exchanger (SHE), gas heat exchanger (GHX), reservoir and absorbent. This system can be grouped into three working circuits called: refrigeration circuit, dissolution circuit and gas circuit. The cycle operates under Dalton's law principle based on partial pressures and the pressure in each point of the system is maintained constant using a gas auxiliary. The DAR system operates in two pressure levels while in operation, similar to a conventional refrigeration system.

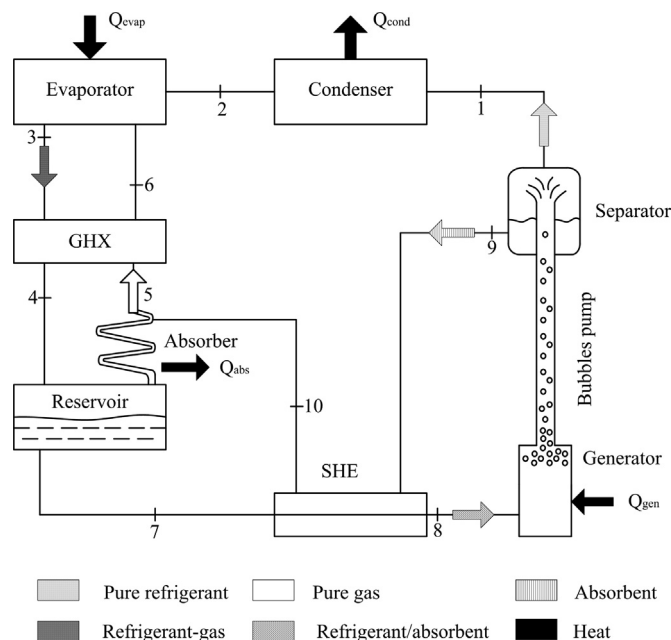


Fig. 1. Refrigeration process for a diffusion–absorption system.

Activation energy for the system,  $Q_{gen}$ , is provided by the generator in order to start heating the solution which is rich in refrigerants and comes from the deposit (8); this results in the formation of vapor bubbles that are dragged through the bubble pump tube with a small amount of liquid, until they are separated. The solution which is poor in refrigerant (9) flows towards the solution heat exchanger (SHE) where it yields heat to the solution rich in refrigerant (7) and is then sent to the absorber (10). The vapor rich in refrigerant (1) is then sent to the condenser, where it is condensed through an exothermal process ( $Q_{cond}$ ), therefore the resulting liquid is introduced in the evaporator (2). Since the evaporator is loaded with gas (6), the liquid's partial pressure diminishes rapidly and as a result low temperature evaporation begins, producing the refrigerant effect,  $Q_{evap}$ . Once out of the evaporator, (3), the mixture of refrigerant and gas flows towards the gas heat exchanger (GHX), whose objective is to reduce the temperature of the gas (4) in order to send it to the deposit. In the absorber, the refrigerant is absorbed by the absorbent, and heat is freed either by cooling water or from the exterior ( $Q_{abs}$ ); since the gas is less dense than the refrigerant, it is separated (5) and sent back to the gas heat exchanger in order to continue the cycle and the refrigerating effect.

Since its invention the diffusion–absorption refrigeration system had been used for small refrigeration capacity units (minibars). Its main benefits are that it does not need a pump to circulate the solution from the absorber to the generator, it does not have mobile parts, and it is noise free, portable, safe and low cost [16]. The generator/bubble pump is the most critical component and the heart of the diffusion–absorption systems. The purpose of this component is to separate the larger amount of the refrigerant from the solution; therefore the efficiency of the system is dependent most of all on the characteristics of the bubble pump [17]. The design and construction of the generators/bubble pump is based on concentric heat exchanger tubes in which the solution rich in refrigerant flows in the inner tube while the poor solution flows in the outer tube. In order to dissipate the heat in the rectifier and condenser, finned tubes are used as heat exchanger equipment. The process of production of cold takes place in the evaporator, which is formed by two coaxial tubes in which the refrigerant and the gas are mixed in a small chamber. Finally, the absorber aims to absorb as much refrigerant as possible. Coaxial exchangers are widely used as heat exchange equipment, and the heat transfer process is done by natural convection with the surroundings (systems cooled by air). In equipments with larger capacity (0.5–3 kW), shell and tubes heat exchangers are also used. They use water as the secondary fluid. In some experimental prototypes the use of plate or coaxial heat exchanger has been introduced to reduce heat loss and size and increase its efficiency, therefore increasing the system's energetic efficiency [18].

## 3. Main working fluids

The  $\text{NH}_3/\text{H}_2\text{O}$  mixture has extended its use in diffusion–absorption refrigeration systems. This is due to the fact that the mixture is chemically stable within a large range of operating pressures and temperatures. Besides, ammonia presents a high latent evaporation heat and a low freezing point ( $-77^\circ\text{C}$ ) making it possible to use it in other applications that require low evaporation temperatures. Since  $\text{NH}_3/\text{H}_2\text{O}$  is volatile, a rectifier should generally be used to separate the water that evaporates with the ammonia, which increases heat loss and reduces the global energy efficiency. Additionally,  $\text{NH}_3/\text{H}_2\text{O}$  has the advantage of not affecting the environment and its production cost is 10–20% less than a synthetic refrigerant [19]; its thermophysical properties

**Table 1**  
Thermophysical properties of inert gases.

| Substance | Specific heat<br>[kJ/kg·K] | Conductivity<br>[W/m·K] | Viscosity<br>[μPa·s] | Density<br>[kg/m <sup>3</sup> ] |
|-----------|----------------------------|-------------------------|----------------------|---------------------------------|
| Hydrogen  | 14.312                     | 0.1769                  | 9.011                | 0.0823                          |
| Helium    | 5.193                      | 0.1553                  | 19.850               | 0.1635                          |
| Neon      | 1.030                      | 0.0493                  | 31.926               | 0.8242                          |
| Argon     | 0.521                      | 0.0177                  | 22.624               | 1.6330                          |

can be obtained from different sources [20–23]. The disadvantage of using  $\text{NH}_3/\text{H}_2\text{O}$  as working fluid is its high operation pressure, toxicity and a corrosive action over copper or copper alloys, limiting its use to materials such as carbon steel.

In diffusion–absorption refrigeration systems, hydrogen is commonly used as an inert gas in order to equilibrate the pressure in the system. An inert gas should comply with the following requirements: very low density and viscosity, low specific heat and thermal conductivity, non-solubility and non-adherence to construction materials [6]. Nevertheless its flammability problems limit the possibility of using this gas beyond the lower cooling capacity of 400 W. In order to exclude these problems and to increase refrigeration capabilities, helium is proposed as an ideal substitute for hydrogen [6,24–27]. Additional noble gases such as neon and argon have also been studied as possible substitutes for hydrogen in these types of applications, resulting in very similar efficiencies to those presented when using the  $\text{NH}_3/\text{H}_2\text{O}/\text{H}_2$  mixture [27].

In Table 1, thermophysical properties of four inert gases are summarized. As can be observed, hydrogen presents the lowest viscosity and density, which reduces internal losses and eases the separation during the absorption process of the mixture. But its higher specific heat and thermal conductivity results in a reduction of its absorption capacities and an increase in heat losses. Even though helium presents almost double the density and has 10 times more viscosity than hydrogen, its lower specific heat and thermal conductivity allows it to absorb a larger amount of refrigerant and reduces internal losses. Although argon and neon can result in an alternative for hydrogen and helium due to their capacities to absorb heat and a very low thermal capacity, they present a low coefficient of heat transfer; they have the disadvantage of being 20 and 10 times more dense, which would lead to problems in the separation process of the mixture (refrigerant/gas) in the absorber.

Even though  $\text{NH}_3/\text{H}_2\text{O}/\text{H}_2$  has been used as a working fluid for many years in diffusion–absorption refrigeration systems, several researches have been done searching for new working mixtures that will minimize activation energy. Pfaff et al. [28] suggest that the  $\text{LiBr}/\text{H}_2\text{O}$  mixture can be used as a working fluid in diffusion–absorption systems. Input temperatures in the generator between 66 °C and 78 °C are needed to activate the bubble pump, making this mixture attractive for solar refrigeration applications.

It is well known that when using water as a refrigerant fluid, its evaporation temperature is limited to values over 0 °C, which results in a viable alternative in air-conditioning applications. The advantage of this mixture is that the absorbent is not volatile; therefore the use of rectifiers such as the one used in  $\text{NH}_3/\text{H}_2\text{O}$  systems is not required. The disadvantage of this mixture is the vacuum pressures. Furthermore, the presence of  $\text{LiBr}$  as an absorbent has crystallization problems in high concentrations. Since salts are highly corrosive, copper needs to be used as construction material for these types of installations. Additives are generally used to avoid corrosion problems and increase heat transfer [29]. Thermophysical properties can be obtained from various sources [30–34].

Binary mixtures of ammonia and some salts have also been studied in order to determine which compound is the most appropriate to reduce activation temperature and increase energetic efficiency [35]. Results show that the  $\text{NH}_3/\text{NaSCN}$  mixture is more efficient than the conventional  $\text{NH}_3/\text{H}_2\text{O}$ . Acuña et al. [36] have incorporated the mixture:  $\text{NH}_3/\text{LiNO}_3$ , and their results confirm that these mixtures reduce activation temperatures. Furthermore, the  $\text{NH}_3/\text{LiNO}_3$  mixtures were approximately 50% more efficient than the conventional  $\text{NH}_3/\text{H}_2\text{O}$ , and 27% more efficient than  $\text{NH}_3/\text{NaSCN}$  for the same operating conditions. Thermophysical properties of  $\text{NH}_3/\text{LiNO}_3$  and  $\text{NH}_3/\text{NaSCN}$  are obtained from the correlations described by Infante Ferreira [37].

Fluoride refrigerants are suggested due to their good solubility with organic solvents such as  $\text{N,N}'$ -dimethylformamide (DMF) and  $\text{N,N}'$ -dimethylacetamide (DMAC). Compared to ammonia, these refrigerants have the advantage of being less toxic, while compared to water, these refrigerants can reach temperatures below 0 °C considered for refrigeration. They are chemically stable, non corrosive, completely miscible in a wide range of temperatures [38,39]. DMF is common and widely used as an absorbent in absorption refrigeration systems and is another compound that has been used in the diffusion–absorption systems. It has a low partial pressure when combined with halogen hydrocarbons. Similar to the  $\text{NH}_3/\text{H}_2\text{O}$  and  $\text{LiBr}/\text{H}_2\text{O}$  mixture, DMF can react with certain metals if oxygen is present, therefore certain precautions must be taken in order to avoid leaks in the system when DMF is used as an absorbent. Properties of halogenated refrigerants combined with DMF have been developed by various researchers [40–43]. Koyfman et al. [44] have conducted an experimental study using R22/DMF as the working fluid. Evaporation temperatures below 0 °C were achieved with activation temperatures in the generator between 50 °C and 90 °C, which led to energetic efficiency of 0.35. Zohar et al. [45] incorporated R32, R124, R125 and R134a refrigerants to their analysis using DMF as absorbent in all cases and their results were valid for different operating conditions. Authors showed that these mixture can be activated at a lower temperature (150 °C), but this is traduced in a lower coefficient of performance and higher condensation and evaporation temperatures when compared to the  $\text{NH}_3/\text{H}_2\text{O}$  mixture.

DMAC is another organic compound that is commercially available and that is considered as one of the absorbents for refrigeration systems due to its good solubility [42]. This compound has been found in the field of diffusion–absorption mixed with halogenated refrigerants. Because there is very little difference in boiling temperatures between both compounds, this results in certain amount of DMAC also being evaporated in the generator, resulting in the need to use a rectifier to avoid the amount of DMAC to be condensed. This results in a loss of cooling capacity and an increase in manufacturing costs. Ezzine et al. [47] show that R124/DMAC is a good working pair because lower vapor pressures than the mixture with DMF and activation temperatures between 80 °C and 180 °C can be obtained, which makes them ideal to be activated with solar energy, geothermal, residual heat or others.

Light hydrocarbons with organic solvents can also be found in literature [46,48]. These mixtures can be activated at temperatures between 120 and 150 °C, but its coefficient of performance is sometimes inferior to those mixtures that have been previously described.

Binary mixtures of 2,2,2-trifluoroethanol (TFE) and tetra ethylene glycol dimethyl ether (TEGDME), also called E18,1 have been theoretically studied in the diffusion–absorption refrigeration systems [49]. This is due to the fact that this compound is very stable, has a low corrosion index and is compatible with materials such as stainless steel and copper. The disadvantages of TFE are its toxicity and flammability but this refrigerant is less toxic than

**Table 2**  
Summary of the characteristics of working fluids.

| Mixture  | Author   | $T_g$ (°C) | Application | COP       | Remarks   |
|--|--|------------|-------------|-----------|---|
| NH <sub>3</sub> /H <sub>2</sub> O/H <sub>2</sub>   | Lin et al. [76] Zohar et al. [54] Starace and De Pascalis [58] Zohar et al. [53] Zohar et al. [27] Zohar et al. [45] | 135–225    | R and AC    | 0.01–0.38 | <ul style="list-style-type: none"> <li>– NH<sub>3</sub> is toxic, and corrosive to copper materials</li> <li>– High operating pressures</li> <li>– Low evaporation temperatures (–77 °C)</li> </ul>   |
| NH <sub>3</sub> /Na <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> H <sub>2</sub> O/NaOH/H <sub>2</sub> | Vicatos [52]   | 137–221    | R           | N/A       | <ul style="list-style-type: none"> <li>– Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> dissolved in water acts as an oxidation inhibitor and reduces water volatility</li> <li>– Activation temperatures lower than the mixture of NH<sub>3</sub>/H<sub>2</sub>O</li> </ul>   |
| TFE/TEGDME/He  | Long et al. [49]   | 100–190    | R           | 0.3–0.56  | <ul style="list-style-type: none"> <li>– Activation temperature lower than the mixture of NH<sub>3</sub>/H<sub>2</sub>O</li> <li>– Less toxic and flammable than the mixture of NH<sub>3</sub>/H<sub>2</sub>O</li> <li>– Does not require a rectifier</li> <li>– Increase in COP of up to 20% when compared to NH<sub>3</sub>/H<sub>2</sub>O</li> </ul> |
| R23/R134a/He   | Wang et al. [69]   | 110–160    | R           | 0.03–0.06 | <ul style="list-style-type: none"> <li>– Lower activation temperatures</li> </ul>   |
| NH <sub>3</sub> + H <sub>2</sub> O + He  | Zohar et al. [27] Acuña et al. [36] Jacob et al. [18] Bourseau and Bugarel [35]                                      | 100–220    | R and AC    | 0.1–0.4   | <ul style="list-style-type: none"> <li>– Increases energetic efficiency</li> </ul>  |
| R22/DMAC/He  | Zohar et al. [45]  | 138–160    | R           | 0.19–0.22 | <ul style="list-style-type: none"> <li>– Requires rectifier</li> <li>– Good solubility with organic solvents</li> <li>– Activation temperature lower than NH<sub>3</sub>/H<sub>2</sub>O</li> <li>– Lower energetic efficiency</li> <li>– Applications for solar refrigeration</li> <li>– Refrigerant GWP equal to 1700</li> </ul>                       |
| R32/DMF/He   | Zohar et al. [45]  | 138–154    | R           | 0.1–0.14  | <ul style="list-style-type: none"> <li>– Requires rectifier</li> <li>– Good solubility with organic solvents</li> <li>– Activation temperature lower than NH<sub>3</sub>/H<sub>2</sub>O</li> <li>– Alternative to solar refrigeration applications</li> <li>– Refrigerant GWP equal to 650</li> </ul>   |
| R124/DMF/He  | Zohar et al. [45]  | 144–160    | R           | 0.14–0.17 | <ul style="list-style-type: none"> <li>– Requires rectifier</li> <li>– Good solubility with organic solvents</li> <li>– Activation temperature lower than NH<sub>3</sub>/H<sub>2</sub>O</li> <li>– Alternative for solar refrigeration applications</li> <li>– Refrigerant GWP equal to 480</li> </ul>  |
| R125/DMF/He  | Zohar et al. [45]  | 143–159    | R           | 0.14–0.16 | <ul style="list-style-type: none"> <li>– Requires rectifier</li> <li>– Good solubility with organic solvents</li> <li>– Activation temperature lower than NH<sub>3</sub>/H<sub>2</sub>O</li> <li>– Alternative to solar refrigeration applications</li> <li>– Refrigerant GWP equal to 2800</li> </ul>  |
| R134a + DMF + He   | Zohar et al. [45]  | 150–160    | R           | 0.16–0.19 | <ul style="list-style-type: none"> <li>– Requires rectifier</li> <li>– Good solubility with organic solvents</li> <li>– Lower activation temperature than NH<sub>3</sub>/H<sub>2</sub>O</li> </ul>  |

|   |   |         |          |           |   |
|---|---|---------|----------|-----------|---|
|   |   |         |          |           | <ul style="list-style-type: none"><li>– Alternative to solar refrigeration applications</li><li>– Refrigerant GWP equal to 1300</li></ul>                   |
| $\text{NH}_3/\text{LiNO}_3/\text{H}_2$                      | Acuña et al. [36] Wang [75]                 | 90–170  | R and AC | 0.156     | <ul style="list-style-type: none"><li>– Better efficiency than <math>\text{NH}_3/\text{H}_2\text{O}</math></li><li>– Does not require a rectifier</li></ul> |
| $\text{C}_4\text{H}_{10}/\text{C}_9\text{H}_{20}/\text{He}$ | Ben Ezzine et al. [46]                      | 120–150 | R and AC | 0.11–0.17 | <ul style="list-style-type: none"><li>– Inflammable</li><li>– High activation temperatures</li><li>– Lower COP</li></ul>                                    |
| R124/DMAC/ $\text{H}_2$                                     | Ben Ezzine et al. [47]                      | 90–180  | R        | 0.05–0.4  | <ul style="list-style-type: none"><li>– Lower vapor pressures</li><li>– Lower activation temperatures than the mixtures with DMF and low GWP</li></ul>      |
| $\text{NH}_3/\text{LiNO}_3/\text{He}$                       | Acuña et al. [36]                           | 110–170 | R        | 0.1–0.39  | <ul style="list-style-type: none"><li>– Use of helium increases COP</li></ul>   |
| $\text{NH}_3/\text{NASCN}/\text{He}$                        | Acuña et al. [36]                           | 115–135 | R        | 0.1–0.45  | <ul style="list-style-type: none"><li>– An alternative to the conventional <math>\text{NH}_3/\text{H}_2\text{O}</math> system with better COP</li></ul>     |
| $\text{NH}_3/\text{NASCN}/\text{H}_2$                       | Acuña et al. [36] Bourseau and Bugarel [35] | 100–150 | R and AC | 0.1–0.6   | <ul style="list-style-type: none"><li>– An alternative to the conventional <math>\text{NH}_3/\text{H}_2\text{O}</math> system with better COP</li></ul>     |

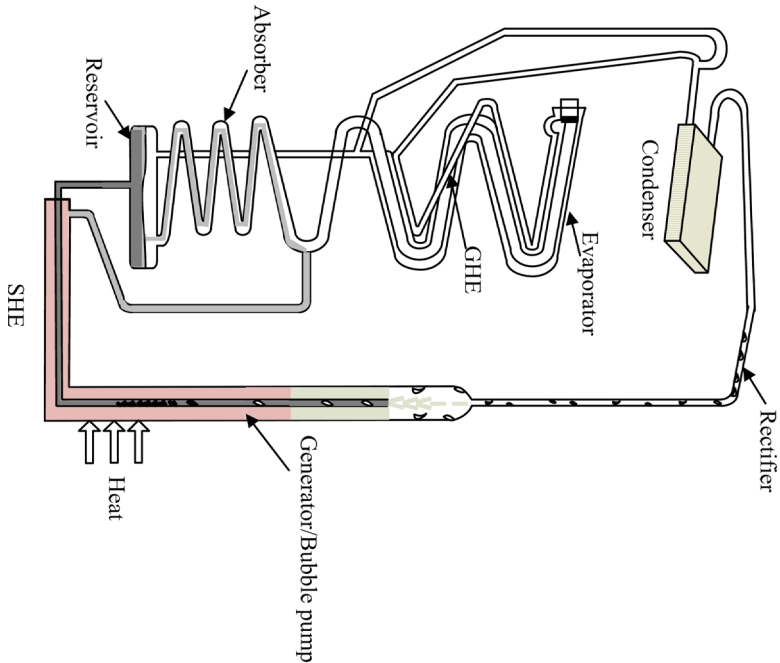


Fig. 2. DAR diagram.

ammonia and does not require the use of a rectifier. The combination of TFE with TEGDME presents a better equilibrium between the liquid–vapor phases. Long et al. [49] have found that the TFE/TEGDME mixture is around 12% more efficient than the conventional ammonia/water mixture. Nevertheless, when the system is cooled with water, activation temperature is reduced to 120 °C and the coefficient of performance increases up to 18%. Evaporation temperatures below 0 °C can be reached by both mixes, but this is reflected in a loss of energetic efficiency in the system.

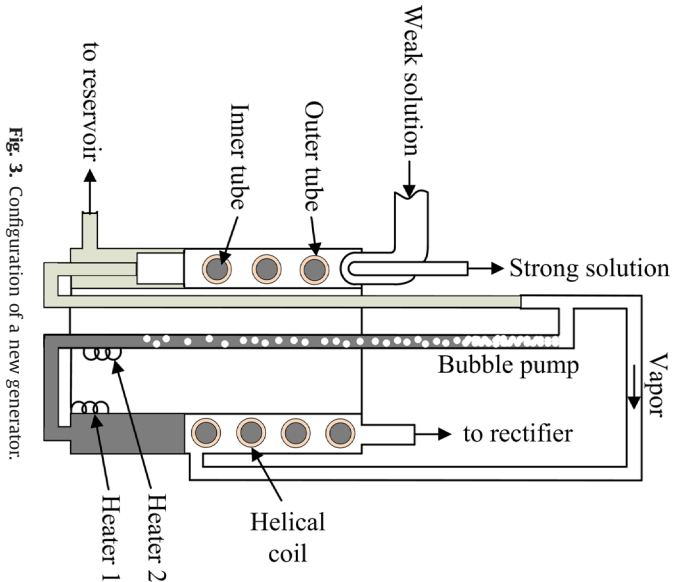


Fig. 3. Configuration of a new generator.



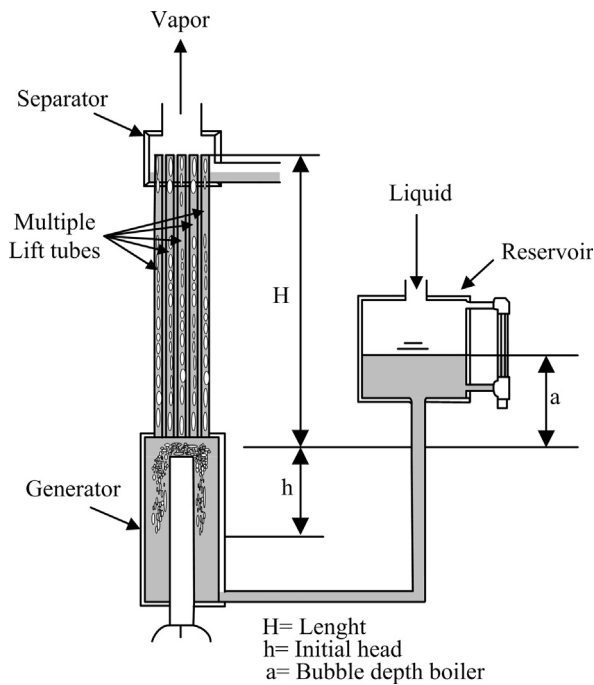


Fig. 4. Configuration of bubble pump with multiple tubes.

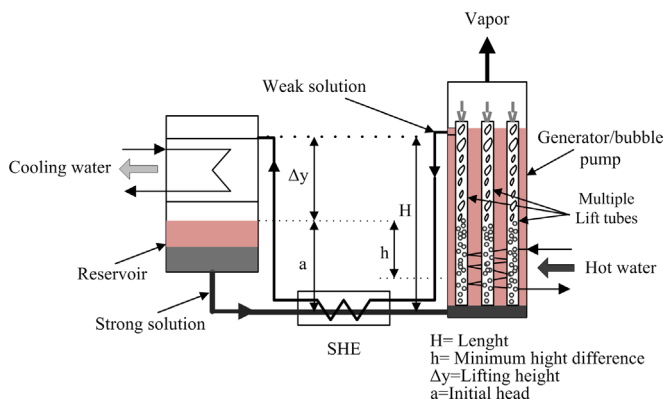


Fig. 5. Generator/bubble pump for solar refrigeration applications.

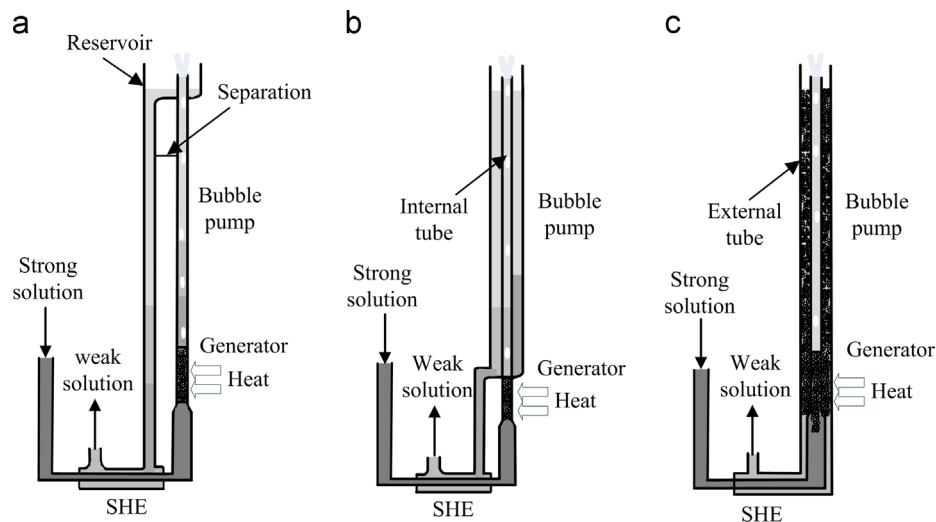


Fig. 6. Different bubble pump configurations.

Values higher than the circulation reason are found for el TFE/TEGDME in a range of activation temperatures from 120 °C to 190 °C, which can result in an increase in the amount of solution flux that flows to the generator and with it an increase in the size of the tubes. Their thermophysical properties can be found in different studies [67,68]. Therefore, a more complete review of working fluids that have been previously described also can be found in the work of Sun et al. [50].

Table 2 shows a summary of working fluids employed in the diffusion–absorption refrigeration systems. Furthermore, it includes the range of activation temperatures ( $T_g$ ), its type of application (R=refrigeration y AC=air-conditioning) and energetic efficiency (COP).

#### 4. Bubble pump configurations

Most of the works related to the diffusion–absorption refrigeration systems have focused on finding the best components and parameters to maximize the energetic efficiency of the system. Fig. 2 shows the first diffusion–absorption refrigeration system, which was introduced to the market by the Electrolux Company in Sweden, also known as Dometic [51]. In this system, the generator and the bubble pump are completely connected; therefore the heat is transferred to the concentric tube that contains the rich solution via the outer tube, on which the poor solution circulates. Furthermore, the condenser is sub-cooled before entering the evaporator, which is coupled to the gas heat exchanger. Even when the system does not use a pump to circulate the solution and the sub-cooling is used, these systems have a low energetic efficiency of about 0.2.

Due to its low efficiency, Chen et al. [9] have developed the configuration of a new generator that increases energetic efficiency in up to 50% (see Fig. 3). Its design combines the generator and the bubble pump to form one component. The proposed generator consists of coaxial tubes with two heating units and the heat from the rectifier is used to preheat the solution, resulting in a reduction of heat loss, increasing the efficiency of the system.

Vicatos and Bannett [52], have conducted experimental work with a diffusion–absorption refrigeration system using a bubble pump with multiple tubes to evaluate its influence on the energetic efficiency of the system (see Fig. 4). Because of the limitations of the unit's components, only a small range of input energy magnitudes were evaluated (400–1000 W). The authors

concluded that the bubble pump with multiple tubes did not limit the speed of the fluid flux and depended exclusively on the amount of heat that was being provided. Furthermore, an increase in the cooling capacity of up to 13% and a lower activation temperature can be obtained when compared to a pump with a single tube.

Fig. 5 shows a generator/bubble pump for solar refrigeration applications that was designed and with which experimental research was conducted [18]. The functioning principle is similar to the configuration studied by Vicatos and Bannet [52], but the difference is that the activation energy is achieved through hot water, which comes from solar collectors, and heat dissipation comes from cooling water. Furthermore, the shell and tubes heat exchanger solution has been replaced for a coaxial heat exchanger solution. Its design allows operating at different temperature ranges and activation energy, reducing heat loss and increasing cooling capacity by 30%, resulting in a more efficient system.

The search to increase the efficiency of the diffusion–absorption refrigeration system motivated Zohar et al. [53] to further research the behavior of three generator/bubble pump configurations (see Fig. 6). In the first configuration (Fig. 6a), the generator and the bubble pump are totally separated, the heat is directly provided to the rich solution without heat transfer to the poor solution, both tubes are isolated to avoid losses. In the second configuration (Fig. 6b), it is partially attached; the heat is supplied to the rich solution through heat transfer from the bubble pump to the outer tube. The outer tube is isolated from its surroundings. In the third configuration both tubes are fully attached (Fig. 6c) and the heat is supplied to the rich solution through the poor solution, and it also separates the refrigerant from the poor solution, which flows from the inferior part of the pump (configuration used in commercial equipment). The authors concluded that the second configuration is more efficient for a same heat flux. Therefore the minimum heat flux should be used to separate the largest amount of refrigerant and obtain an increase in the energetic efficiency of the system.

Using a totally separated bubble pump configuration, Ezzine et al. [46] experimented with a diffusion–absorption refrigeration system cooled by air and using a mixture of light hydrocarbons ( $C_4H_{10}/C_9H_{20}$ ) as a working fluid and helium as an auxiliary gas. The maximum COP obtained was 0.17 with a heat input of 275 W and an evaporation temperature of 9 °C.

Based on the reviewed literature it was found that experimentally, the rectifier is one of the components that also affects energetic efficiency of the system; nevertheless, most of the works are dedicated to research and modeling the generator/bubble pump in order to optimize the design and the separation process for the mixture. An opportunity opens for further research regarding new designs, or component modeling, such as heat exchangers, searching for optimal design configurations that are more effective and that will result in a significant improvement in the global efficiency of diffusion–absorption systems.

## 5. Modeling of the diffusion–absorption cycles

Modeling has become a very important tool in evaluating the energetic behavior of equipment or global systems in the area of diffusion–absorption refrigeration. Thermodynamic or physical models based on equation of mass, energy and species conservation are the most developed and available in literature [35,36,53,55–57]. These models are based on non-linear equation systems that are obtained from the characterization of each of the components that are part of the system. Among the most used software for programming these types of models are EES<sup>®</sup> (Engineering Equation Solver) and Matlab<sup>®</sup>. Since the works that have been mentioned before

present a model based on equations for conservation of mass and energy and considering operating parameters, this leads to a deviation of theoretical results between 20 and 30% (due to loss of energy) when compared to experimental results [17]. Starace and De Pascalis [58] therefore developed a new model which considers heat loss in the generator. Their results adequately predict the system's behavior, obtaining a deviation of only between 2 and 8%. Other models consider a larger number of input parameters, which allow describing the operation conditions of the diffusion–absorption cycle in a more realistic manner.

Because the bubble pump is the main component in the diffusion–absorption refrigeration system, it has been found from the experimental point of view that this equipment is more efficient in the slug type flux regime [60], furthermore the diameter of the generator's tube is restricted to the use of Chisholm's equation [61], which establishes the transition between the slug to the churn flux regime.

Other authors have developed models based on mass, momentum and energy conservation equations to obtain optimal [10] and the minimum required heat flux to activate the bubble pump under different operating conditions [11,12]. Flux patterns and change of phase conditions are considered through the bubble pump tube that makes it possible for the model to make an approximation to real conditions. Nevertheless, the inconvenience is that it is done under conditions of adiabatic flux. For that reason, computational tools such as CFD (Computational Fluid Dynamics) can be a viable alternative to design and escalate these systems. This is primarily due to the fact that CFD is a robust tool that combines VOF (Volume of Fluid) model to study complex change of phase phenomena, heat and mass transfer, which has been used to predict void fraction and in this way understand flux conditions that develop within the system [70–72].

Thermodynamic model evaluates the energetic behavior of the system either globally or individually (each equipment); input operating conditions are supposed in most of the models, therefore the results can either be closer or distant from those which were obtained through experimentation, depending on the number of restrictions that the model imposes.

In general, this type of models analyzes geometrical parameters, such as diameter and length of the tube, submergence ratio and driving head. Flux patterns and energy transfer in the bubble pump are also studied.

## 6. Current developments and trends

Energetic and environmental sustainability in the field of cold generation (refrigeration) places diffusion–absorption refrigeration systems as an attractive technology in refrigeration and air conditioning applications. Regarding refrigeration, commercial systems are limited to cooling capacity of no more 400 W. Additionally it is difficult to find commercial air-conditioning and refrigeration equipment with cooling capacity between 1 kW and 5 kW, available in the market. For this type of application conventional systems (vapor compression) are commonly used, but they have the disadvantage of increasing environmental problems and an overload of the electrical network, therefore positioning the development and application of diffusion–absorption systems for cooling capacities 1–5 kW.

According to the reviewed literature, an additional current trend is the development of alternate systems that can be activated with residual or solar energy [59]. Considering diffusion–absorption technology as a viable proposal, some works have been analyzed both theoretically and experimentally with commercial refrigerators with small cooling capacities and activated with solar energy [7,62,63], their energetic efficiency being a

common denominator. In Educational Institutions experimental prototypes were designed for cooling capacity of 2.5 kW with applications of solar climatization [64–66].

In terms of working mixtures, substances that can reduce the activation temperature of the system are being used, obtaining an increase in the use of solar energy for this type of technology for sustainable systems in the fields of refrigeration and air-conditioning.

The use of refrigerating mixtures can be considered as a viable option regarding this trend [35,36,49], mainly because the use of a rectifier is not required. Besides, the mixtures are studied in order to analyze their influence on the energetic efficiency of the system. Needless to say some mixtures that have been studied are composed of substances which possess high values of global warming potential [45–47,69], therefore this work considers the search or development of substance with a low global warming potential, according to the trends in the use of fluids in the field of refrigeration [73].

Recently, an experimental study that incorporates an ejector over the line of refrigerating gas at the exit of the evaporator resulted in an increase in energetic efficiency of the system, generating energy saving of up to 20% under operating conditions [74]. It is evident that research will continue regarding new configurations that will help improve the efficiency, which is the main disadvantage of this technology.

## 7. Conclusions

A review of the state of the art of the diffusion–absorption refrigeration technology has been presented in this work, starting with the onset of this technology including refrigeration processes, main working fluids, basic equipment and current trends.

It can be concluded that the technology is attractive since it has benefits when compared to conventional vapor compression of small cooling capacity because they do not have mobile parts, avoid noises and represent a lower cost in the market. Nevertheless it has been demonstrated that this technology is around 40% less efficient than conventional absorption systems.

From the various works that were analyzed it can be concluded that the most important parameters that affect energetic efficiency of the system are the flux regime, activation heat, diameter and length of the bubble pump, and submergence ratio.

Commercially the most common working mixture is ammonia/water with hydrogen or helium as an auxiliary gas. Nevertheless different mixtures are studied in order to obtain increased efficiency and find different sources of input energy, such as solar. It is intended to further divulge this technology and motivate research interest and the search for energy efficiency.

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